Preparation and characterization of porous Si₃N₄ ceramics prepared by compression molding and slip casting methods

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Abstract. Porous silicon nitride (Si₃N₄) ceramics were fabricated by compression molding and slip casting methods using petroleum coke as pore forming agent, and Y₂O₃–Al₂O₃ as sintering additives. Microstructure, mechanical properties and gas permeability of porous Si₃N₄ ceramics were investigated. The mechanical properties and microstructure of porous Si₃N₄ ceramics prepared by compression molding were better than those which were prepared by slip casting method, whereas slip casting method is suitable for the preparation of porous Si₃N₄ ceramics with higher porosity and excellent gas permeability.

Keywords. Porous Si₃N₄ ceramics; preparation; microstructure; mechanical properties; gas permeability.

1. Introduction

Porous ceramics are used as filters, catalyst carriers or as insulators at high temperatures (Haslam *et al* 2000; Oh *et al* 2000; Corbin *et al* 2001). Recently, applications for separation filters have become important to reduce environmental pollution in various fields. One of the most important properties of porous ceramics for filters is permeability because this property directly correlates with the pressure drop during filtration. Porous Si₃N₄ is a prominent filtering material due to its excellent mechanical, high-temperature thermal and chemical stability (Kawai and Yamakawa 1997; Shigegaki *et al* 1997). However, porous ceramics require higher porosity to reach the required permeability (Glass and Green 1999; Tomita *et al* 2005) and this causes lowering of the mechanical properties (Kani *et al* 1991; Nishikawa *et al* 2001; Ashizuka *et al* 2002). Thus, preparing porous ceramics which satisfy both high permeability and high mechanical strength is difficult by conventional porous ceramic processing. Because these properties are strongly influenced by the microstructure, controlling the microstructure of porous ceramics is essential. The development of porous Si₃N₄ ceramics with a fibrous interlocking offers the advantage of high strength and toughness (Yang *et al* 2001a,b, 2003).

Recently, many studies have been devoted into the molding methods of porous Si₃N₄ ceramics. Shigegaki *et al* (1997) employed silicon nitride whiskers as the starting materials and a tape-casting method as the alignment technique. The fabricated specimen with 14% of porosity showed a microstructure with rod-like grains preferentially aligned toward casting direction, and exhibited high strength of ~1 GPa. Yang *et al* (2001a) fabricated porous Si₃N₄ ceramics with a high porosity of 50–60%, a very small linear shrinkage of ~2–3%, and strength of ~100 MPa. Fukasawa *et al* (2002) fabricated porous silicon nitride with the porosity of >50% by freeze drying method. Porous Si₃N₄ ceramics with a porosity of 70–75% and strength of 5–8 MPa were reported by Shan *et al* (2005a). Later, Ohji (2008) fabricated Si₃N₄ ceramics with a porosity of 0–30% by using partial hot-pressing process. The dimension of manufacturing products prepared by compression molding with one-step forming is relatively accurate, which is advantageous in producing articles with accurate dimension. However, the manufacturing efficiency is relatively low, more importantly and geometry of the shaped articles is quite simple, which is disadvantageous in producing articles with complex shape. So many people have paid much more attention to slip casting recently (Moreno *et al* 1999). Slip casting has been reported as a simple and inexpensive consolidation process to produce materials with high green density and homogenous microstructure even for complex geometries (Xu *et al* 2003a,b). However, a pure Si₃N₄ suspension was not well-dispersed and stable because of its grain size, morphology, isoelectric point and other properties (Penas *et al* 2001), and other low density grains can improve the properties of suspension, such as petroleum coke. Meanwhile, petroleum coke is cheaper and a more easily attainable pore forming agent than organic whiskers and active carbon, and it has good stability in aqueous medium (Shan *et al* 2005b). Besides, sintering additive is also an important factor to be considered. Y₂O₃ and Al₂O₃ have been used to fabricate porous Si₃N₄ ceramics

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because of the related glass phase (Xu *et al* 2006; Belmonte *et al* 2008). The sintering additive accelerates the growth of β-Si$_3$N$_4$, which may improve mechanical properties of the materials.

From these viewpoints, porous Si$_3$N$_4$ ceramics were fabricated by compression molding and slip casting methods using petroleum coke as pore forming agent, and Y$_2$O$_3$–Al$_2$O$_3$ as sintering additives. Microstructure, mechanical properties and gas permeability of porous Si$_3$N$_4$ ceramics were investigated in the present study.

2. Experimental

2.1 *Preparation of samples*

Commercially available Si$_3$N$_4$ powder (Shanghai Junyu Co. Ltd., Shanghai, China; α-Si$_3$N$_4$ ratio: > 95%, median particle size: 1·2 μm, main impurities by weight: O = 1·6%; C < 0·2%; Cl, Fe, Ca, and Al$_2$O$_3$ < 80 ppm) was selected for use in this work. 5 wt. % Y$_2$O$_3$ (99·99% purity, Shin-etsu Chemical Co. Ltd., Tokyo, Japan) and Al$_2$O$_3$ (99·99% purity, Wenzhou Jingjing Aluminum Oxide Co. Ltd., Wenzhou, China; median particle size: 3·6 μm) were used as sintering additives. Petroleum coke (Changsha Xunyi Chemical Co. Ltd., Changsha, China; C: 97·3% D_{50}: 10 μm, main impurities by weight: S <0·5%; Si <0·08%; V <0·015%; Fe <0·08%) was added as a pore forming agent. Content of petroleum coke and Al$_2$O$_3$ was varied from 10–50 wt. % and 2–4 wt. %, correspondingly. Different amounts of test samples were used such as: (S1) 10 wt. % petroleum coke + 2 wt. % Al$_2$O$_3$, (S2) 20 wt. % petroleum coke + 2·5 wt. % Al$_2$O$_3$, (S3) 30 wt. % petroleum coke + 3 wt. % Al$_2$O$_3$, (S4) 40 wt. % petroleum coke + 3·5 wt. % Al$_2$O$_3$ and (S5) 50 wt. % petroleum coke + 4 wt. % Al$_2$O$_3$.

Simultaneous differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA) were conducted to investigate discharge temperature of petroleum coke in a TGA–DSC apparatus (SDT Q600, TA Co., Ltd., America) under flowing air atmosphere.

The different powder mixtures were wet-milled in methanol for 24 h, using high-purity Si$_3$N$_4$ media. The obtained slurry was dried and sieved through a 150 μm screen. The mixed powders were then pressed under 20 MPa, to form rectangular bars measuring $55 \times 6 \times 5$ mm^3.

An aqueous suspension of Si$_3$N$_4$/petroleum coke and sintering additive powder mixtures with a solid content of 56·20 wt. % was prepared by planetary milling for 2·5 h in a polyethylene bottle, using 0·30 wt. % carboxymethyl cellulose (CMC) (viscosity, 800–1200 mPa·s) as binder, and 0·05 wt. % glycerol as anti-blowing agent. The pH of suspension was adjusted to 10–10·5 using NH$_4$OH. The corresponding viscosity was measured using a rotational viscometer (NDJ-1, Shanghai Jingke Industrial Co., Ltd.,

China) at 12 r.p.m. Drain casting was performed in a gypsum mold after aging for 12 h, and subsequently dried at 60°C for 10 h to remove moisture.

The green bodies prepared by compression molding and slip casting methods were first thermally discharged at 650°C with a heating rate of 30°C/h to remove petroleum coke. Subsequently, the discharged bodies were put into a BN-coated graphite crucible and sintered in a graphite resistance furnace (High multi-5000 Fujidempa Co. Ltd., Osaka, Japan) at 1750°C for 2 h in a nitrogen atmosphere of gas pressure, 0·225 MPa.

2.2 *Examination of properties*

The bulk porosities were measured by the Archimedes displacement method. The microstructure was characterized by a scanning electron microscope (SEM, model JSM-35C, JEOL, Tokyo, Japan). The three-point bending strength was measured on sample bars with a span of 16 mm at a crosshead speed of 0·5 mm/min by an Instron 1195 instrument (Instron Co., Buckinghamshire, England).

The permeability of porous ceramics was evaluated using (1) (Isobe *et al* 2007):

$$\Delta P = \frac{\eta L}{\mu A} Q, \tag{1}$$

where ΔP is the pressure drop from entrance to exit of the sample, μ the Darcy permeability, η the dynamic viscosity of the fluid, A and L are the cross-sectional diameter and the thickness of the sample, Q the flow rate. The samples cut into 0·5–2 mm in thickness (10 mm Ø in diameter) were fixed in the centre of an epoxy resin mold. ΔP and Q were measured using similarity equipment. The gas permeametry equipment used in this study is shown in figure 1 (Isobe *et al* 2007). The apparatus comprises an inner pipe and an outer pipe which are arranged coaxially, a gas inlet for admitting a flow of air get into a first space, and pressure difference (DP) measuring systems for measuring a pressure difference, ΔP, between said first space (P1) and a second space (P2) comprising the interior of the inner pipe. Q is obtained by Flow meter.

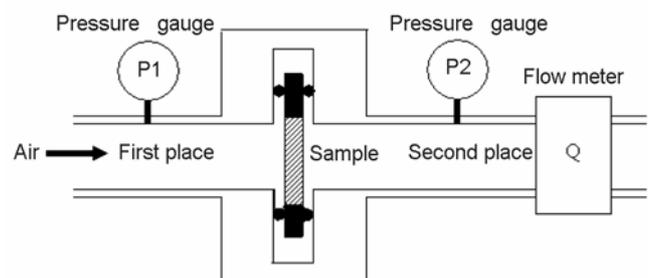**Figure 1.** Schematic model of equipment for gas permeability.

The permeability is calculated from the slope of the line plotted for ΔP vs Q using (1). The dynamic viscosity, η, of air as used for the calculation was $1 \cdot 8 \times 10^{-5}$ Pa·s.

3. Results and discussion

3.1 *TGA–DSC analysis*

The thermal analysis results of petroleum coke are shown in figure 2. It can be seen that the weight loss happened at 600°C which was due to the carbon combustion derived from petroleum coke. With carbon combustion, heat was generated, which would support combustion of the residual carbon in petroleum coke. As a result, there was no need to increase the temperature to 850°C at which the weight loss was most. In order to burning out petroleum coke in green bodies, the discharging temperature was at 650°C for 3 h.

3.2 *Microstructure*

Figure 3 shows SEM micrographs of porous Si$_3$N$_4$ ceramics prepared by compression molding and slip casting method. There were some obvious large pores and numerous small pores distributed in the matrix region. It was reasonably believed that small pores originated from interlocking of rod-like β-Si$_3$N$_4$ grains, and that the large pores were formed by the burning-out of petroleum coke out of samples. Figure 4 shows the green body discharged at 650°C with a heating rate of 30°C/h for removing petroleum coke, and there were many obvious large pores formed by the burning-out of petroleum coke ($D50 = 10$ μm).

Compared with figures 3 (a) and (b), no large elongated grains were observed in (c) and (d), whereas it is striking that (a) and (b) had an amount of finer, higher aspect ratio of β-Si$_3$N$_4$ grains. The explanation for the microstructural formation of Si$_3$N$_4$-based materials can be given by the following two reasons: firstly, β-Si$_3$N$_4$ grains with a higher aspect ratio will yield in the liquid phase with a higher viscosity during sintering, because the grain growth in Si$_3$N$_4$-based materials is diffusion controlled and can be considered in terms of Ostwald ripening (Hwang *et al* 1998). The higher viscosity hinders both the heterogeneous nucleation of the grains and the material transport by means of diffusion during solution-reprecipitation, and thus it can promote preferential growth of the pre-existing intrinsic β-Si$_3$N$_4$ grains. However, in the aqueous slips, it was reasonably believed that a little Si$_3$N$_4$ powder was hydrolyzed and transformed into SiO$_2$, which was in agreement with the results of Zhang *et al* (2005). With the amount of SiO$_2$ on Si$_3$N$_4$ surface increasing, the liquid phase formed by the sintering additives and amount of SiO$_2$ on Si$_3$N$_4$ surface had a lower eutectic temperature and liquid viscosity during sintering, the lower viscosity helped to attain heterogeneous nucleation, so the heterogeneous nucleation rate was higher than that of grains growth during sintering, so the aspect ratio of porous Si$_3$N$_4$ grains prepared by slip casting method is lower than that of compression molding.

3.3 *Mechanical properties*

Figure 5 showed the porosity and flexural strength of porous Si$_3$N$_4$ ceramics prepared by compression molding and slip casting methods. The flexural strength of porous Si$_3$N$_4$ ceramics with a porosity of 28·85–39·79% prepared by compression molding method was in the range of 136·75–223·82 MPa, and that the flexural strength of porous Si$_3$N$_4$ ceramics with a porosity of 40·05–58·62% prepared by slip casting method was varied from 61·58–159·65 MPa. The porosity of porous Si$_3$N$_4$ ceramics increased proportionally with increasing contents of petroleum coke and Al$_2$O$_3$, but the porosity of porous Si$_3$N$_4$ ceramics prepared by compression molding method was lower than that of slip casting method. And the flexural strength of porous Si$_3$N$_4$ ceramics decreased with the increase of porosity. Since porosity and mechanical properties usually are contradictory, it was understandable that increasing of porosity resulted in the degradation of mechanical properties. Furthermore, a function can be used to express the relation between strength and porosity (Coble and Kingery 1956):

$$\sigma = \sigma_0 \exp(-\beta P), \tag{2}$$

where σ_0 is the strength at a porosity of 0, β the structural factor, and P the porosity. The strength decreases exponentially with porosity.
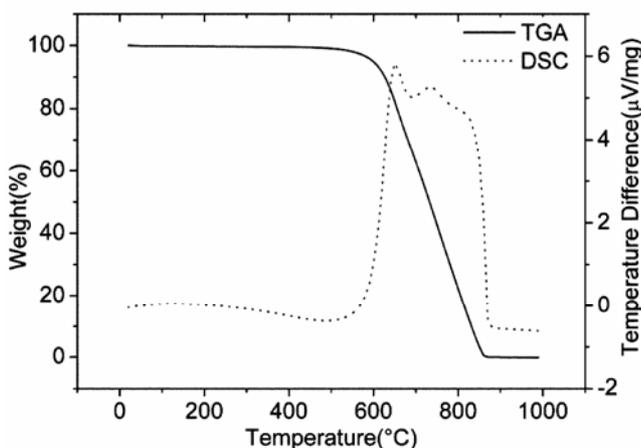
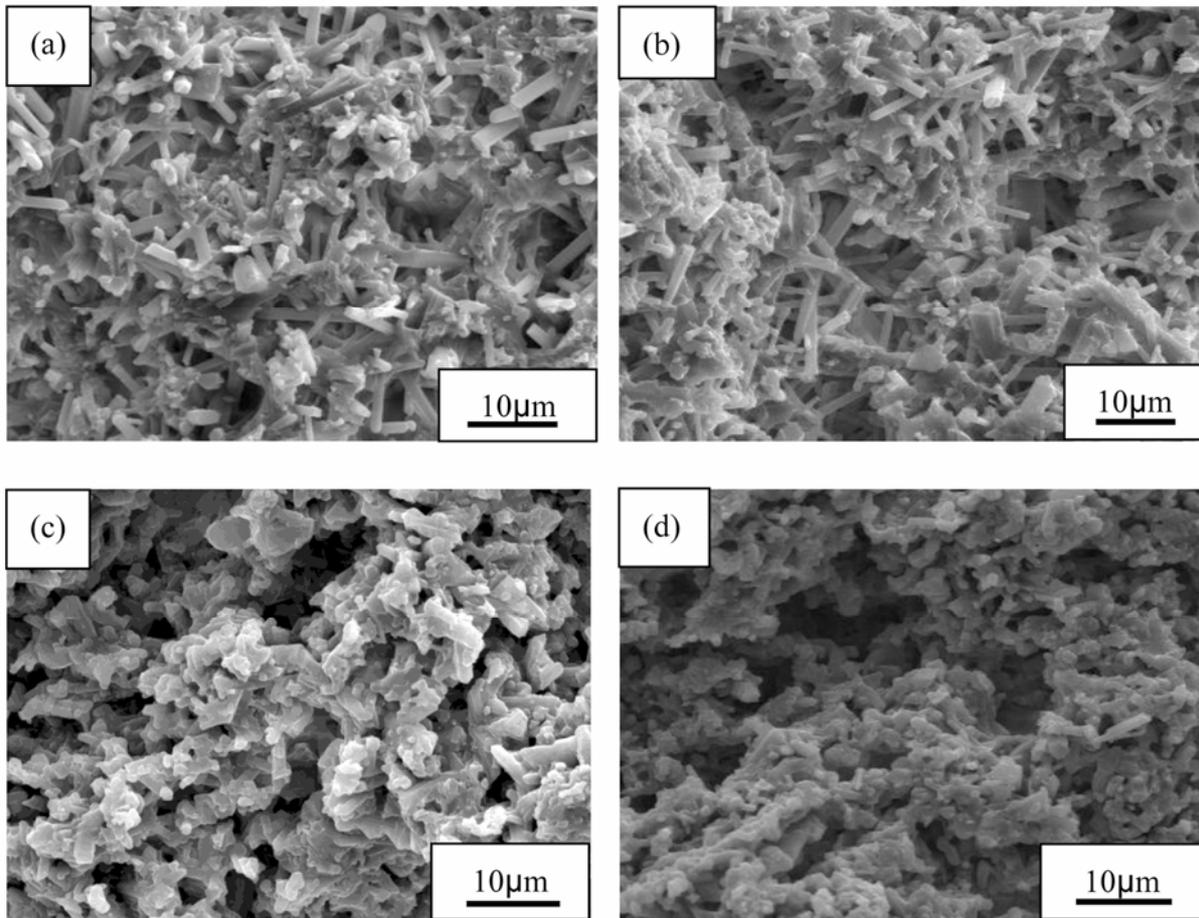**Figure 2.** TGA and DSC curves of petroleum coke discharged in a TGA–DSC apparatus under flowing air atmosphere.

Figure 3. SEM micrographs of porous Si_3N_4 ceramics prepared by compression molding and slip casting methods:
(**a**) S2-Compression molding, (**b**) S4-compression molding, (**c**) S2-slip casting and (**d**) S4-slip casting.
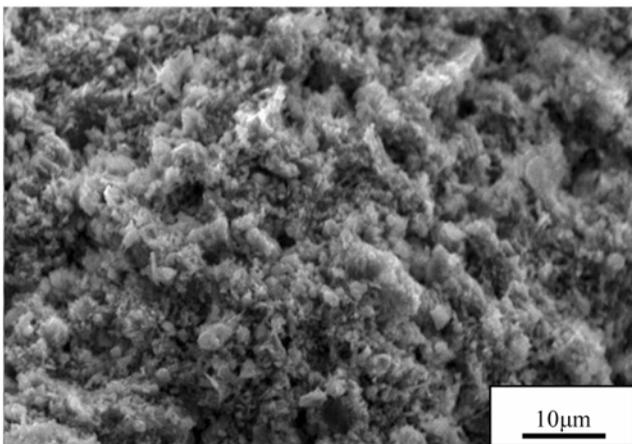

Figure 4. SEM micrographs of the green body after discharging petroleum coke.
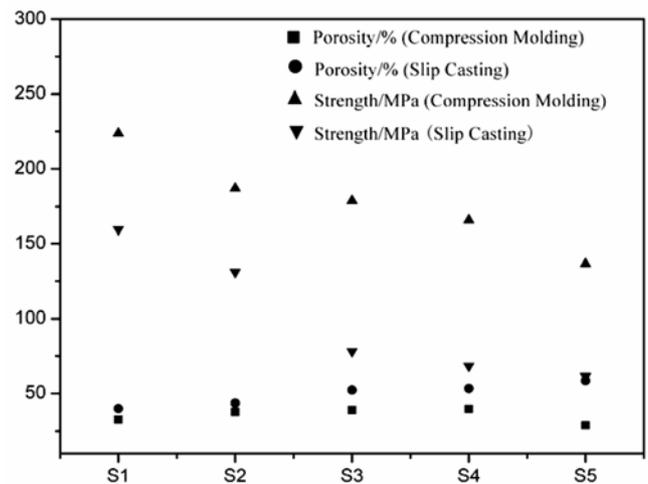

Figure 5. The porosity and flexural strength of porous Si_3N_4 ceramics prepared by compression molding and slip casting methods.

However, compared with slip casting method, porous Si_3N_4 ceramics prepared by compression molding method exhibited outstanding mechanical properties at similar porosity. The higher flexural strength can be attributed to the well-developed and high aspect ratio of β-Si_3N_4 grains, which was in agreement with the results of microstructure.

3.4 *Gas permeability*

Figure 6 shows Darcy permeability (K) of porous Si_3N_4 ceramics. Darcy permeability (K) of porous Si_3N_4 ceramics prepared by compression molding method was in the range of $(1 \cdot 01–1 \cdot 97) \times 10^{-13} \, m^2$, and that Darcy permeability (K) of porous Si_3N_4 ceramics prepared by slip casting method was varied from $3 \cdot 36 \times 10^{-13} \, m^2$ to $6 \cdot 43 \times 10^{-13} \, m^2$. Darcy permeability ($K$) decreased first then increased with increasing addition of petroleum coke and Al_2O_3. This result may be attributed to the distributions of small pores originating from interlocking of rod-like β-Si_3N_4 grains and large pores formed by burning-out petroleum coke in porous Si_3N_4 ceramics. It was reasonably explained that small pores in samples S1 and S2 played a leading role in the process of gas permeability, which was not completely straight and bent at the points connected by the contact of original petroleum coke. In this way, fluid flow was thought to suffer from some resistance and lower permeability occurred at those points. However, with petroleum coke content in the samples S3, S4 and S5 increasing, large pores increased, fluid flow did not suffer from some resistance and go through straight, and it was considered that gas permeability strongly depended on large pores, so Darcy permeability (K) increased. Darcy permeability (K) of porous Si_3N_4 ceramics prepared by slip casting was higher than that of compression molding method because of higher porosity. Gas permeability of porous materials is closely related to the open porosity and size, the higher the porosity and size, the larger Darcy permeability (K). However, the porosity and mechanical properties usually are contradictory, if porous ceramics require higher porosity for good gas permeability to reach the demand, this causes lowering of the mechanical properties, porous Si_3N_4 ceramics with synergy of strength and permeability
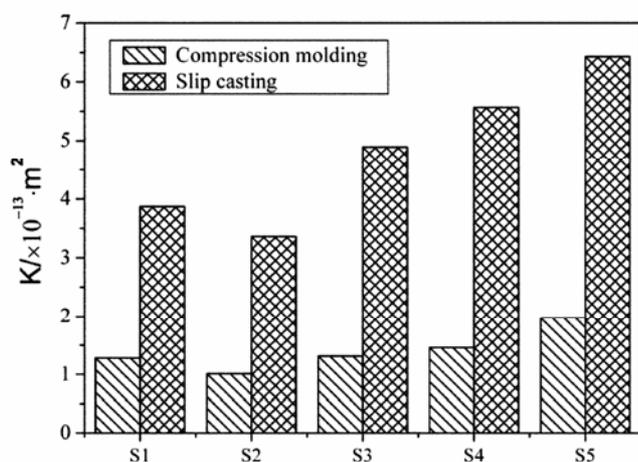
can be considered. Compression molding method is suitable for the preparation of porous Si_3N_4 ceramics with a relative lower porosity and gas permeability but higher flexural strength, whereas slip casting method using petroleum coke as pore forming agent, and Y_2O_3–Al_2O_3 as sintering additives is a promising preparation route for porous Si_3N_4 ceramics with higher porosity and excellent gas permeability.

4. Conclusions

Porous Si_3N_4 ceramics were fabricated by compression molding and slip casting methods using petroleum coke as pore forming agent, and Y_2O_3–Al_2O_3 as sintering additives. Microstructure, mechanical properties and gas permeability of porous Si_3N_4 ceramics were investigated. The mechanical properties and microstructure of porous Si_3N_4 ceramics prepared by compression molding were better than those prepared by slip casting method, but gas permeability was contrary. Compression molding method is suitable for the preparation of porous Si_3N_4 ceramics with a relative lower porosity and gas permeability but higher flexural strength, whereas slip casting method is a promising preparation route for porous Si_3N_4 ceramics with higher porosity and excellent gas permeability.

Figure 6. Darcy permeability (K) of porous Si_3N_4 ceramics prepared by compression molding and slip casting methods.

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